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I also certify that by virtue of an assignment registered under the Patents Act 1977, the application is now proceeding in the name as substituted.

I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General

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Signed, *Andrew Garside*

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GB9917583.8

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of

Incorporated in the United Kingdom
MARCONI CASWELL LTD
One Bruton Street
LONDON
IX 8AQ
United Kingdom

Incorporated in the United Kingdom

[ADP No. 07806326001]

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1st 1977

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Request for grant of a patent

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The Patent Office

 Cardiff Road
 Newport
 Gwent NP9 1RH

1. Your reference

9917583.8

28 JUL 1999

2. Patent application number

(The Patent Office will fill in this part)

3. Full name, address and postcode of the or of each applicant (*underline all surnames*)

Marconi Electronic Systems Ltd

 The Grove
 Warren Lane
 Stanmore
 Middx

SECTION 30 (1977 ACT) APPLICATION FILED 28.01.00

Patents ADP number (*if you know it*)

7607948001

If the applicant is a corporate body, give the country/state of its incorporation

ENGLAND

4. Title of the invention

Hydrocarbon Fuel Processor Catalyst

5. Name of your agent (*if you have one*)

R K Telfree

Colin Francis Haste

5/1/27
5/15/00d
JM

"Address for service" in the United Kingdom to which all correspondence should be sent (*including the postcode*)

GEC PATENT DEPARTMENT
WATERHOUSE LANE
CHELMSFORD
ESSEX CM1 2QX
Patents ADP number (*if you know it*)

40261005 / 40527004

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (*if you know it*) the or each application number

Country

Priority application number
(*if you know it*)Date of filing
(*day / month / year*)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(*day / month / year*)8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (*Answer 'Yes' if:*

YES

- a) *any applicant named in part 3 is not an inventor, or*
 - b) *there is an inventor who is not named as an applicant, or*
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Patents Form 1/77

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Priority documents	0
Translations of priority documents	0
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	4 ✓
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Any other documents (please specify)	0

-
11. I/We request the grant of a patent on the basis of this application.

Signature
R K Tolfree

Date
26th July 1999

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12. Name and daytime telephone number of person to contact in the United Kingdom

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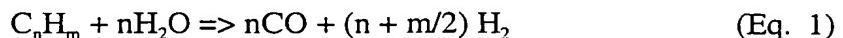
HYDROCARBON FUEL PROCESSOR CATALYST

This invention relates to a hydrocarbon fuel processor catalyst for converting or reforming a hydrocarbon fuel into a simple fuel and is more especially concerned with a catalyst for converting a hydrocarbon fuel to hydrogen for use in a fuel cell.

5 Fuel cells offer the promise of smaller and lighter weight power sources that are potentially instantaneous and silent in their operation. For mobile applications, such as vehicular power sources, polymer fuel cells have been proposed in which a polymer conducts protons. Due to their relatively low operating temperature (typically around 80°C), such cells offer a rapid start up as required in these applications. For larger scale, 10 generally static applications, solid oxide fuel cells are known which use a solid oxide of zirconium and rely on oxygen ion conduction. Due to their higher operating temperature, typically around 800°C, such fuel cells are able to utilise more complex fuels such as methanol, methane or natural gas. Whilst suitable for large scale operation, such as combined heat and power facilities for building complexes, these cells are not suited to 15 mobile applications as they are bulky and have a slow start up due to their high operating temperature. In both cases fuel cells require a simple fuel, most typically pure hydrogen in the case of a polymer fuel cell, instead of the more widely available and comparatively more stable heavier hydrocarbon fuels such as diesel. A fuel processor or reformer transforms one form of hydrocarbon fuel into the simpler fuel.

A number of different designs of fuel processor have been proposed for converting diesel fuels to hydrogen which are based on a steam-reforming reaction in which vaporised hydrocarbon fuel is reacted with steam. This reaction can be represented by the following endothermic equation:

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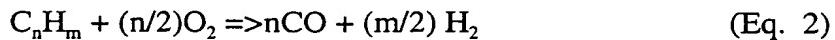


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A catalyst may optionally be used to increase the reaction rate, though high temperatures and pressures are still required. As can be seen from the equation, the carbon in the hydrocarbon fuel is converted to carbon monoxide by oxidation using the oxygen provided by the steam whilst the hydrogen in the fuel and steam is released as hydrogen gas. The optimum steam to carbon ratio (S/C) depends on the processor conditions (temperature and pressure), but invariably this ratio increases as the carbon content of the hydrocarbon increases. Large quantities of steam are therefore required for heavy fuels such as diesel and this demands a high energy input to vaporise the water, leading to a poor thermal efficiency, a slow response time and slow start up from cold.

20



The optimum oxygen to carbon ratio (O/C) depends on the processor conditions and increases as the carbon content of the hydrocarbon increases. Again a catalyst can be used to increase the reaction rate. To prevent clogging of the catalyst, most typically by

coke deposition, the initial combustion can occur at high temperatures in the absence of a catalyst to break the diesel fuel down to simpler molecules. The gas stream is then passed over a catalyst to further break down the molecules into carbon monoxide and hydrogen. Although such a processor exhibits a faster response it has a relatively lower

5 hydrogen conversion efficiency than a steam reforming system.

It has been further proposed to provide fuel processors which use an "auto thermal reforming process" to convert the hydrocarbon fuel to hydrogen and carbon monoxide with a combination of the above two processes. In such a processor the heat liberated by

10 the exothermic partial oxidation reaction (Eq. 2) is used to drive the endothermic steam reforming reaction (Eq. 1) thereby improving the overall thermal efficiency of the processor. Different specialist catalysts may be used in physically separate partial oxidation and steam reforming reaction volumes within the processor or alternatively the partial oxidation and steam reforming reactions can take place over a common catalyst
15 bed. The latter produces a simpler system design but places great demands on the catalyst material. In one known design the vaporised fuel is mixed with air and steam and then injected into an enclosure containing the granulated catalyst material.

At present the known fuel processors capable of processing heavier hydrocarbons fuels
20 such as diesel are not ideally suited to small scale mobile applications. Firstly, the endothermic nature of the steam generating and steam reforming processes does not readily lend itself to operating efficiently on a small scale. Secondly, the comparatively high carbon content (high carbon to hydrogen ratio C/H) of many hydrocarbon fuels such as diesel clogs the catalyst through the deposition of coke (carbon) on the surface of the

catalyst which blocks access to the active surface of the catalyst. Thirdly, the high sulphur level in many heavier hydrocarbon fuels poisons, that is reduces the activity of, the known catalysts used in the steam-reforming process thereby degrading the conversion efficiency.

5

The known catalysts for fuel conversion, or reforming, comprise base metals (such as nickel), noble metals (such as platinum), or a mixture of these, either in powdered form or as a coating on the surface of an inert ceramic substrate. The noble metal is generally dispersed in the form of small particles in order to minimise the metal cost and maximise the surface activity. These catalysts are however, adversely affected by sulphur present in the fuels and are vulnerable to coking since there is no mechanism to remove the carbon from the catalyst surface once it has been deposited.

A need exists therefore for a catalyst which at least in part overcomes the limitation of 15 the known hydrocarbon fuel processor catalysts. The present invention has arisen in an endeavour to develop a new catalyst formulation which is suitable for use with diesel and other heavy hydrocarbon fuels in an autothermal fuel processing system and which is resistant to both sulphur poisoning and clogging with coke deposition.

20 According to the present invention a hydrocarbon fuel processor catalyst comprises a rare earth metal cobalt oxide ($MCoO_3$) having the perovskite crystal structure. Due to its high oxygen ion mobility at temperatures at which such fuel processors operate, typically less than 800°C, such a catalyst offers a number of advantages over the known catalysts: (i) the presence of the oxygen ions at the catalyst surface coating promotes the fuel

breakdown process; (ii) the oxygen ions oxidise any carbon or contaminants which may be deposited on the catalyst surface coating during the fuel breakdown reaction and this reduces the likelihood of the catalyst becoming clogged, especially when using a high C/H fuel such as diesel, and (iii) the oxygen ions prevent contaminants which might

5 otherwise de-activate the catalyst, such as sulphur, becoming bonded to the surface coating. The inventors further believe that during the use of the catalyst the surface decomposes and becomes covered with a catalytically active coating of rare earth oxide, hydrated rare-earth oxide and cobalt metal particles which prevents the catalyst's activity becoming rapidly degraded by carbon deposition and/or by the effects of sulphur or other
10 contaminants. A catalyst in accordance with the invention can therefore be said to be self cleaning. In contrast the known catalysts comprise an inert support structure with a catalytically active coating which is vulnerable to the effects of carbon and/or sulphur.

Advantageously the catalyst further includes a noble metal or noble metal oxide. Such
15 a catalyst offers a high catalytic activity in which the oxygen ions provide a scouring activity which protects the activity of the noble metal or noble metal oxide at the operating temperature of the fuel processor. In one embodiment the noble metal or noble metal oxide comprises platinum or platinum oxide. In a particularly preferred embodiment the noble metal or noble metal oxide comprises ruthenium or ruthenium
20 oxide which is found to give at least the same activity but which has a cost appreciably less than that of platinum. Preferably the noble metal or noble metal oxide is present up to 2 mole %.

Preferably the catalyst further comprises a solid solution having the perovskite crystal structure of the rare earth metal cobalt oxide and an alkaline earth metal cobalt oxide, such as for example a solid solution of lanthanum cobalt oxide and strontium cobalt oxide. The substitution of the rare earth ions by alkaline earth ions increases the number

5 of vacant sites for oxygen within the perovskite crystal structure thereby increasing the number and the mobility of oxygen ions within the crystal lattice. Advantageously the alkaline earth metal cobalt oxide is included in a proportion of up to 50%.

10 In a preferred catalyst composition the alkaline earth metal comprises strontium although calcium or barium can be used.

According to a further aspect of the invention a hydrocarbon fuel processor for converting a hydrocarbon fuel to hydrocarbon incorporates a catalyst as described above.

15 According to a yet further aspect of the invention there is provided use of a catalyst as described above in a hydrocarbon fuel converter for converting a hydrocarbon fuel to hydrogen.

Nine catalyst compositions in accordance with the invention will now be described by
20 way of example only. The first catalyst composition described is lanthanum cobalt oxide (LaCO_3) having the perovskite crystal structure. Lanthanum oxide (La_2O_3) powder was heated in air at 1000°C to decompose any Lanthanum Hydroxide La(OH)_3 present in the material to give single phase La_2O_3 . The single phase La_2O_3 material was mixed with cobalt oxide (CoO) powder in appropriate weights to give the LaCoO_3 and the mixture

ball-milled for 4 hours in approximately 40 gram batches and then calcined (heated in a furnace) in air at 1050°C for 3 hours. The ceramic product after calcining was crushed and graded into a desired particle size, approximately 1-10µm, prior to testing. As will be appreciated by those skilled in the art, the desired particle size will depend on the type

5 of fuel processor and can accordingly be readily optimised for a required application.

X-ray diffraction studies of the material showed the crystal structure to be a substantially

phase pure perovskite crystal structure. The perovskite crystal structure is that which

exists in mineral perovskite CaTiO_3 and which is commonly adopted in compounds

10 having the general formula ABO_3 where A is a relatively large cation (lanthanum in this

example) and B is a relatively smaller cation (cobalt in this example). The B cations are

each surrounded by a maximum of six oxygen ions to form a three-dimensional network

of corner shared octohedra whilst the A cations occupy the interstices between the

octohedra. The facile mixing of cations with different valences on both the A and B sites

15 combined with the variable valence nature of the B cations promotes a complex defect

structure which can provide a high mobility for the oxygen ions. X-ray diffraction

patterns of samples showed that a significant quantity of La_2O_3 still remained in the

samples which could not be eliminated by calcining for longer periods. This is believed

to be a consequence of the CoO actually being a mixture of CoO and Co_3O_4 , the latter of

20 which cannot be readily converted to single CoO by heat treatment. To compensate for

this a 5 mole % excess of CoO was added to the starting mixture. Samples prepared in

this way showed only a trace of La_2O_3 remaining in the final composition.

Testing of the catalyst with diesel fuel in a fuel processor showed the material to have good catalytic activity which was resistant both to clogging by coke or other contaminants and to poisoning from sulphur. The inventors believe that the improved catalytic properties are due to its high oxygen ion mobility at temperatures for use in such

5 fuel processors, typically less than 800°C. A catalyst in accordance with the invention therefore has the following advantages: (i) the presence of the oxygen ions at the catalyst surface promotes the fuel breakdown process, (ii) the oxygen ions oxidise any carbon or contaminants which may be deposited on the catalyst surface during the fuel breakdown reactions thereby reducing the likelihood of catalyst clogging, especially
10 when using a fuel having high carbon to hydrogen ratio such as diesel, and (iii) the oxygen ions prevent contaminants, such as sulphur, becoming bonded to the surface which might otherwise deactivate the catalyst.

15 It is also believed that during the use of the catalyst a certain degree of decomposition of the perovskite crystal structure occurs at the material surface such that the surface of the material becomes covered with a catalytically active coating of lanthium oxide (La_2O_3), hydrated lanthanum oxide and cobalt metal particles which prevents the catalyst's activity becoming rapidly degraded by carbon deposition and/or by the effect of sulphur or other contaminants.

20

Eight other catalyst compositions were synthesised which are shown in Table 1 below. First, samples were prepared containing the noble metals ruthenium (Ru) and platinum (Pt) by calcining mixtures of La_2O_3 , and PtO_2 or RuO_2 with a 5 mole % excess of CoO (compositions 2 and 3 in the table). Scanning electron microscopy analysis of the

platinum oxide and ruthenium oxide powders showed that it was an extremely fine powder with a primary particle size probably well below $0.1\mu\text{m}$ (dimensions beyond the resolution of the scanning electron microscope equipment available at the time of analysis). The energy-dispersive X-ray analysis in a scanning electron microscope of

5 single grains of the resultant catalyst material confirmed that the platinum/ruthenium was present either within the grains or as a coating on the surface of the grains. No particles could be identified which were very rich in platinum/ruthenium, suggesting that the noble metal is not present as a second phase (either as the metal or as the oxide).

10 Catalysts containing the noble metal and/or noble metal oxide were found to exhibit an enhanced activity compared to LaCoO_3 . This is attributed to the catalytic activity of the noble metal which is protected against clogging and or contamination by the scouring effect of the high mobility oxygen ions from the LaCoO_3 perovskite crystal structure.

15 This being said it will be appreciated that the concentration of noble metal is selected such that there is sufficient LaCoO_3 to provide adequate cleaning of the metal. Test results indicate that ruthenium is at least as effective as platinum but has the substantial advantage of being much lower in cost.

20 In the remaining compositions (4 to 9), a fraction of the lanthanum ions was replaced by strontium (Sr) ions to form a solid solution of LaCoO_3 and SrCoO_3 . A 5 mole % excess of CoO was also added to the starting mixtures of these compositions. The calcination temperature needed for the complete elimination of La_2O_3 decreased as the strontium content increased, and was found to be 950°C for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$. The complete list of synthesized samples is given in Table 1. The substitution of the lanthanum ions by

strontium ions increases the number of vacant sites for oxygen within the perovskite structure thereby increasing the number and the mobility of oxygen ions within the crystal lattice.

5 It will be appreciated that the present invention is not limited to the specific compositions described and that further compositions are envisaged which are within the scope of the invention. For example the basic catalyst has been described in relation to LaCoO_3 , though other rare earth metal (M) cobalt oxides (MCoO_3) having the perovskite crystal structure could be used. Furthermore it is envisaged to add other noble metals or noble 10 metal oxides or a mixture thereof. Furthermore it will be appreciated that solid solutions with alkaline earth metals other than strontium such as calcium or barium can be used to increase the oxygen ion mobility. Furthermore it will be appreciated that a catalyst in accordance with the invention can be used for other types of hydrocarbon fuels other than diesel and is especially suited to use with heavier hydrocarbon fuels.

Composition 1 LaCoO_3	Composition 4 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$	Composition 7 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$
Composition 2 LaCoO_3 + 2 mole % PtO_2	Composition 5 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ + 2 mole % PtO_2	Composition 8 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ + 2 mole % PtO_2
Composition 3 LaCoO_3 + 2 mole % RuO_2	Composition 6 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ + 2 mole % RuO_2	Composition 9 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ + 2 mole % RuO_2

Table 1: Catalyst compositions

CLAIMS

1. A hydrocarbon fuel processor catalyst comprising: a rare earth metal cobalt oxide having the perovskite crystal structure.

2. A catalyst according to Claim 1, and further including a noble metal or noble metal oxide.
3. A catalyst according to Claim 1 or Claim 2, which comprises a solid solution having the perovskite crystal structure of the rare earth metal cobalt oxide and an alkaline earth metal cobalt oxide.
4. A catalyst according to any preceding claim, wherein the rare earth metal is lanthanum.
5. A catalyst according to any one of Claims 2 to 4, wherein the noble metal or noble metal oxide is ruthenium or ruthenium oxide.
6. A catalyst according to any one of Claims 2 to 4, wherein the noble metal or noble metal oxide is platinum or platinum oxide.
7. A catalyst according to Claim 3 or to any one of Claims 4 to 6 when dependent on Claim 3 wherein the alkaline earth is calcium, strontium or barium.

8. A catalyst according to Claim 3 or any one of Claims 4 to 7 when dependent on Claim 3, and including the alkaline earth metal cobalt oxide in a proportion up to 50%.

9. A catalyst according to Claim 2 or any one of Claims 3 to 8 when dependent on Claim 2 and comprising including, the noble metal or noble metal oxide up to 2 mole %.
10. A catalyst having a composition substantially as described with reference to any of the examples of Table 1.
11. A hydrocarbon fuel processor for converting a hydrocarbon fuel to hydrogen incorporating a catalyst according to any preceding claim.
12. Use of a catalyst according to any preceding claim in a hydrocarbon fuel converter for converting a hydrocarbon fuel to hydrogen.
13. Use according to Claim 12 wherein the catalyst undergoes thermal decomposition such that its surface becomes coated with catalytically active lanthium oxide, hydrated lanthium oxide and cobalt metal particles.